# Organic Halogen and Hydrocarbon Distributions During SEAC4RS Measured from the ER-2 and DC-8:

comparison with the CAM-Chem model.

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INTRODUCTION: Organic halogens and hydrocarbons are important contributors to chemical processes in the upper troposphere/lower stratosphere (UTLS) region and hydrocarbons are well known contributors to chemical processes throughout the troposphere. Their geographic and vertical distributions are influenced by emission sources, photochemical processing and atmospheric transport. These forcing factors are variable over region and season.

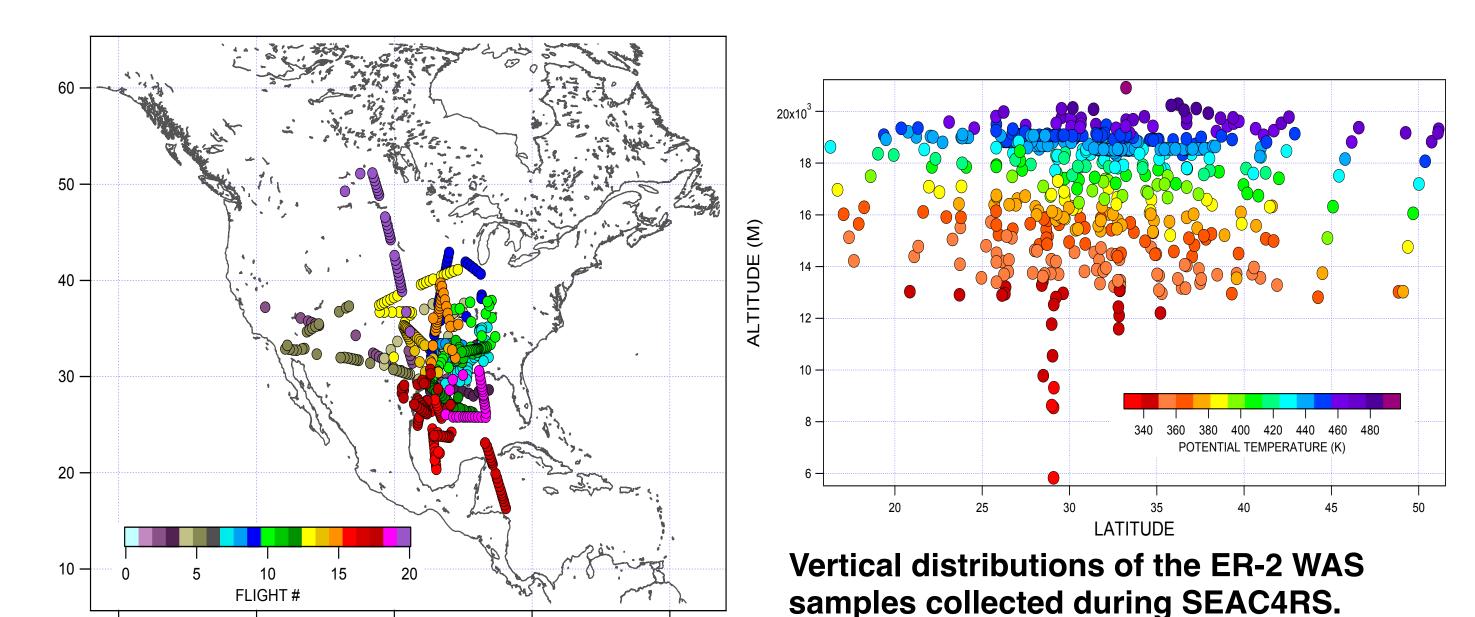
The Studies of Emissions and Atmospheric Composition, Clouds, and Climate Coupling by Regional Surveys (SEAC4RS) campaign, carried out in August-September 2013, allowed us to investigate distributions of trace gases in the UT/LS during the late summer/early fall season and to characterize trace gas relationships during this period.

Whole Air Sampler systems (WAS) were deployed during SEAC4RS on the NASA ER-2 (Univ. of Miami WAS) and the NASA DC-8 (Univ. of California, Irvine WAS). Both systems measured a wide variety of organic halogen and hydrocarbon species in the samples collected on 18 ER-2 research flights and 21 DC-8 research flights.

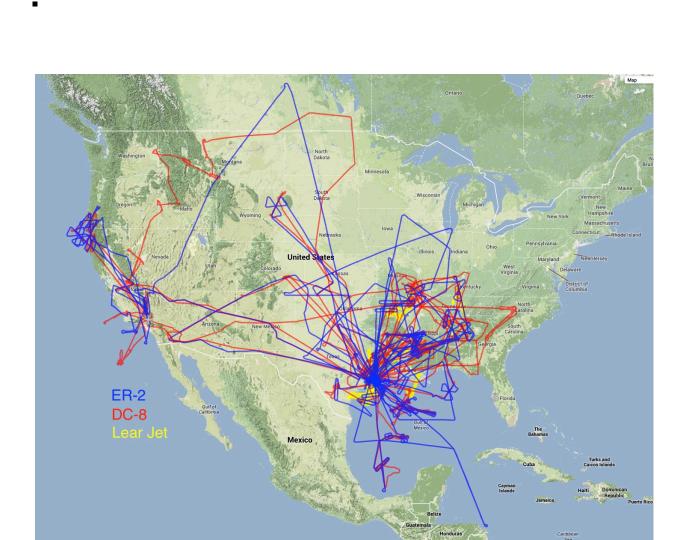
The ER-2 sample collection focused on obtaining measurements near and above the tropopause at altitudes from 6 to 19 km with a specific focus of sample collection during the vertical profiles near the tropopause. A total of 545 samples were collected from the ER-2. The DC-8 covered the 0-12km altitude range and sampling strategy was based on the specific science goals for a given flight. A total of about 2,800 samples were collected from the DC-8.

ER-2 WAS samples were shipped to the Univ. of Miami for analysis and the DC-8 samples were shipped to Univ. of California, Irvine for analysis. Both laboratories use multiple gas chromatographs with a variety of detectors.

For this presentation we show the vertical distributions of select chemical species from the surface to the lower stratosphere and compare those distributions to the Community Atmosphere Model with Chemistry (CAM-Chem) in order to evaluate their representation in the global model.



**WAS** sample locations of 18 ER-2 research



SEAC4RS ER-2, DC-8, and Lear jet flight tracks.

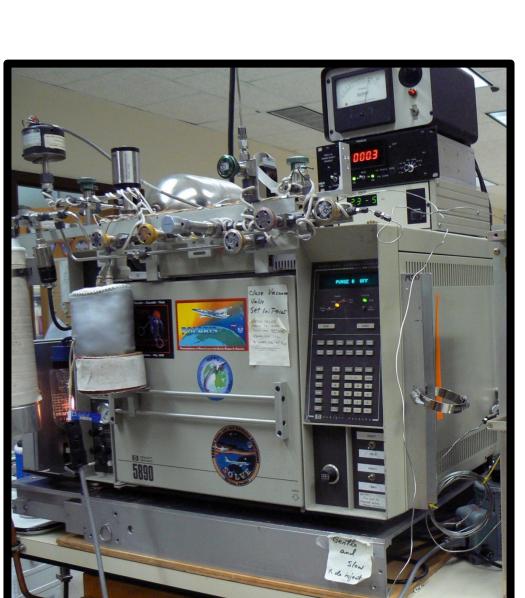
- **Vertical distributions of the DC-8 WAS** samples collected during SEAC4RS.

#### The ER-2 Whole Air Sampler (WAS) includes:

- 32 sample canisters -1.5 liters each
- Metal valves open with external motors 4-stage Metal Bellows
- Computer controller



WAS system located in the belly pod of the ER-2 aircraft. Insert: Canisters used in the WAS being prepared for flight. Actual configuration in the pod is a single length of about 2 x 16 canisters.



One of the GC-MSD instruments used for the analysis of halocarbons, hydrocarbons, organic nitrates and others at UM.

<b>Longer Lived Species</b>		<b>Longer Lived Species</b>			<b>Shorter Lived Species</b>			
Chlorofluorocarbons	Yrs	S	Solvent	Yrs	S	Organic nitrates	Yrs	S
CFC-11	50	Α	Carbon Tetrachloride	40	Α	Methyl nitrate	0.08	A/N
CFC-12	102	Α	Methyl chloroform	4.8	Α			
CFC-113	85	Α				Non- Methane Halocarbons		
CFC-114	300	Α	Other			Ethane (C2H6)	0.2	
			Methane	9 N	I/A/B	Ethyne	0.06	<b>A</b> /
Halons			Methyl Chloride	1.5	N/B	Propane	0.04	
Halon 1211	20	Α				Benzene	0.04	A/
Halon 2402	20	Α	<b>Shorter Lived Spec</b>	<u>cies</u>		i-Butane	0.02	
						n-Butane	0.02	
Hydrochlorofluorocarb	ons/		Solvents					
Hydrofluorocarbons			Methylene Chloride	0.3	Α	Others		
HCFC_141b	9.4	Α	Chloroform	0.4	A/N	1,2 dichloro ethane	0.3	
HCFC_22	13	Α	Tetrachloroethylene	0.3	A			
HCFC_142b	19.5	Α	,					
HCFC _134a	14	Α	Methyl Halides			6		
HCFC_152a	1.5	Α	Bromoform	0.1	N	Source		rial
HCFC_124	5.9	Α	Methyl Bromide	0.8 A	/N/B	A= antropogenic/indu N= natural/marine		IIai
HCFC_123	2	Α	Methylene Bromide	0.4	N	B=Biomass burn		
			•	0.01	N			
			CHxBryClz	0.1	N			

Partial list of target gases measured from the UM Whole Air Sampler system with lifetimes and major

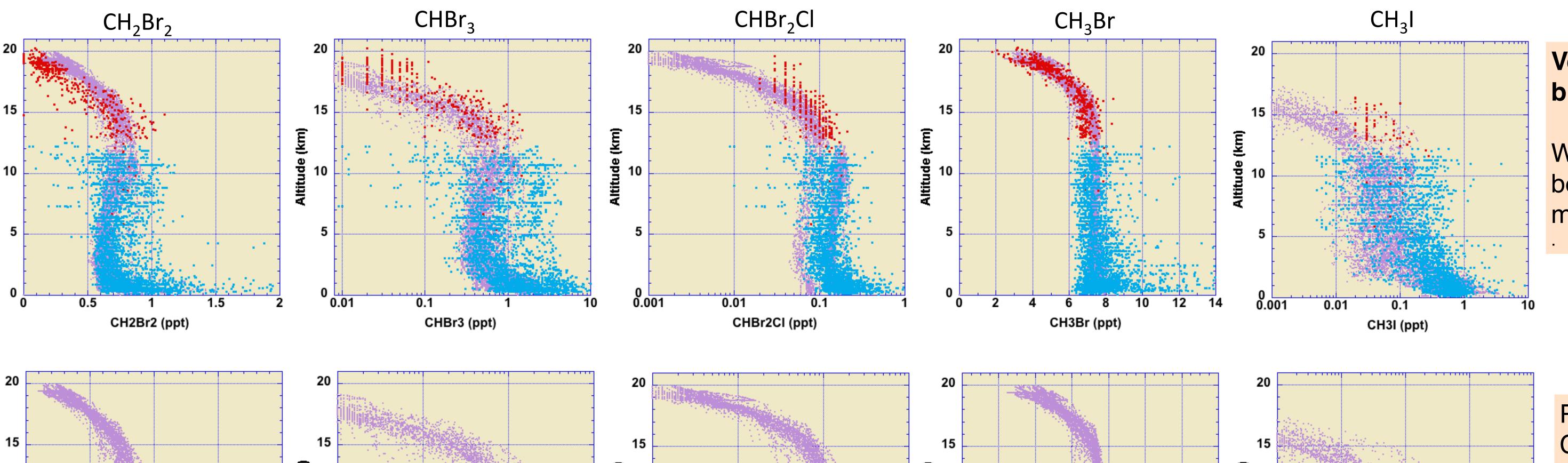
Figures below show the complete data sets of SEAC4RS (Aug-Sept., 2013) WAS data from: the ER-2 (red) and the DC-8 (blue)

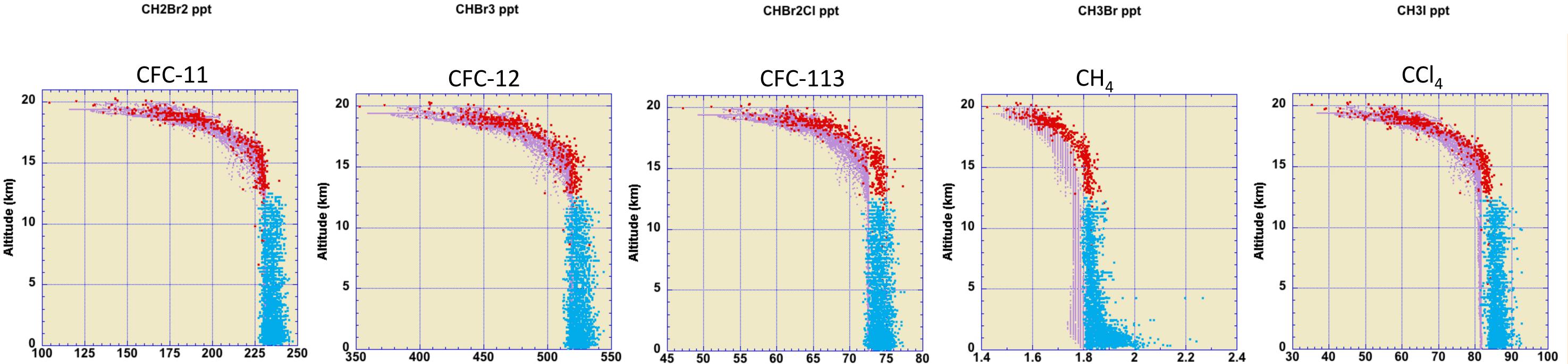
Compared with output corresponding to the ER-2 and DC-8 flight tracks from the: CAM-Chem model (purple)

#### **CAM-Chem details:**

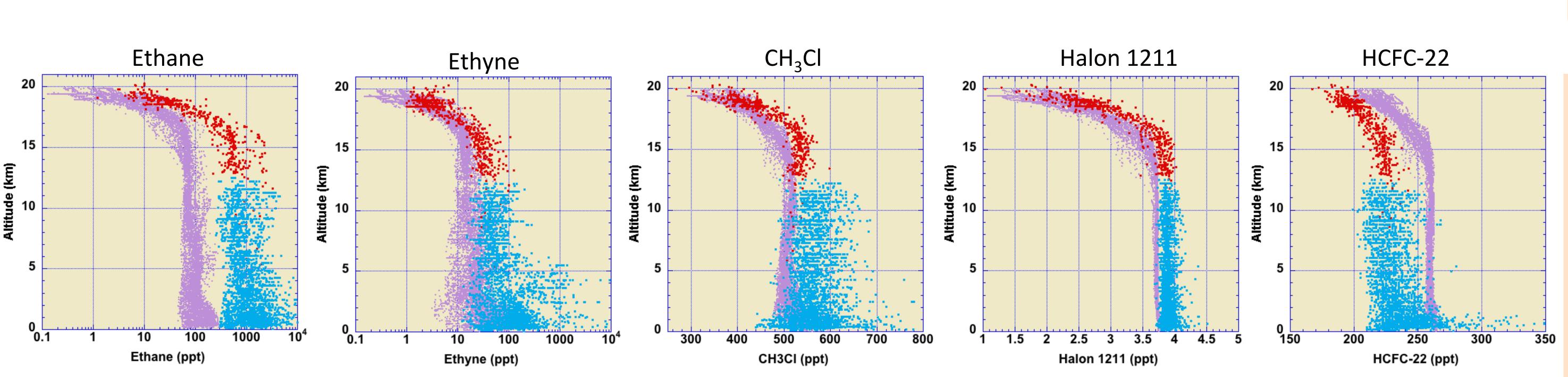
Organic halogens: Baseline mixing ratios from WMO 2010 assessment. 1° resolution CH4: Baseline mixing ratios from Meinhausen et al., 2011, RCP6.0 after 2005. Specified dynamics from MERRA 56 levels from surface to 40 km VSL chemistry from Ordonez et al., 2012 and Saiz-Lopez et al., 2014.

### The combined data sets provide a consistent picture of the trace gas distributions over the SEAC4RS domain from near surface to 19+ km, which allows an unprecedented comparison with CAM-Chem.





CFC-113 (ppt)





WAS system on the DC-8.

CFC-11 (ppt)

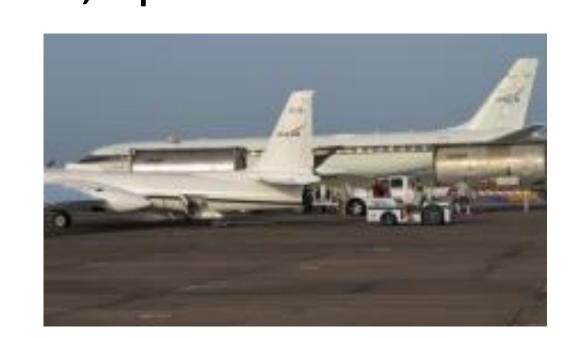
CFC-12 (ppt)

NASA DC-8 aircraft.

For CH<sub>3</sub>Cl and halon 1211, the discrepancies between tropospheric measurements and model are due to boundary conditions in the model, which were based on WMO 2010 projected mixing ratios for 2013. The measured values are consistent with NOAA surface measurements during the SEAC4RS time period. In addition, CH3Cl seasonality is not included in the model, so we will investigate the impact of that for the SEAC4RS time period.

CH4 (ppt)

HCFC-22 surface NH value was calculated as 5% higher than the WMO 2010 global average projected for 2013 to reflect the NH/SH gradient seen in HIPPO WAS measurements. While the gradient is accurate for 2013, the boundary condition mixing ratio for HCFC 22 was too high. Observed mixing ratios are consistent with NOAA surface measurements.







**Results and Discussion** 

## Very short lived organic bromine and iodine species.

We see excellent agreement between the measurements and model.

Panels to the left show CAM-Chem output only. These plots correspond to the CAM-Chem output plotted under the measurements in the panels above.

#### CFCs, methane (CH₄), and carbontetrachloride (CCI<sub>4</sub>)

We see excellent agreement in the profile shapes between the measurements and model. The discrepancies between tropospheric measurements and model are due to boundary conditions in the model, which were based on WMO 2010 projected mixing ratios for 2013. The measured values are consistent with NOAA surface measurements during the SEAC4RS time period.

### Ethane, Ethyne, Methyl Chloride, Halon 1211, and HCFC-22

We see excellent agreement in the profile shapes between the measurements and model. However, for ethane, the model is significantly lower than the measurements. Emissions from the oil and gas industry may be too low in the model and Nicola Blake (UC Irvine) and Louisa Emmons (NCAR) are evaluating this. For ethyne, the model is also lower than the measurements and we will assess our emission inventories for this

compound as well.